

**SYNTHESIS AND CHARACTERIZATION OF
POLY(ETHYLENE OXIDE) (PEO) - BASED AND
POLYACRYLONITRILE (PAN) - BASED POLYMER ELECTROLYTES
TO BE USED IN PHOTOELECTROCHEMICAL (PEC) SOLAR CELLS**

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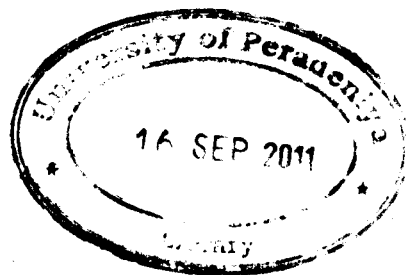
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AND POLYACRYLONITRILE (PAN) - BASED POLYMER ELECTROLYTES
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Dye sensitized photo-electrochemical (PEC) solar cells require solid state redox electrolyte systems with good conductivity, mechanical strength and chemical stability. Iodide ion containing polymer electrolytes are important as redox species in PEC solar cells as well as in iodide ion conducting batteries and other devices. In this work, ionic conductivity and thermal, dielectric and transport properties of some Polyethyleneoxide (PEO) and Polyacrylonitrile (PAN) based electrolyte systems and their applications in PEC solar cells were studied.

Solid polymer electrolyte membranes were prepared by complexing tetrapropylammonium iodide ($\text{Pr}_4\text{N}^+\text{I}^-$) and PEO. The PEO: $\text{Pr}_4\text{N}^+\text{I}^- + \text{I}_2 = 9:1$ ratio gave the best room temperature conductivity for the electrolyte. For this composition, by incorporating the plasticizer ethylene carbonate (EC), a conductivity enhancement of four orders of magnitude was obtained. A marked conductivity enhancement was observed during the melting of the polymer crystallites and above this polymer melting temperature (T_m) the conductivity reached values of the order of $10^{-3} \text{ S cm}^{-1}$. The T_m decreased from 66.1 to 45.1 °C and the glass transition temperature (T_g) decreased from -57.6 to -70.9 °C due to the incorporation of the EC. The room temperature dielectric constant increased from 3.3 for the unplasticized sample to 17.5 for the plasticized sample. It can be inferred from the dielectric results, that the iodide ion is well dissociated and despite its large size and relatively low concentration it is a relatively efficient charge carrier. All solid solar cells were fabricated with plasticized electrolytes containing PEO: $\text{Pr}_4\text{N}^+\text{I}^- + \text{I}_2 = 9:1$ and EC. Maximum photocurrent of $98 \mu\text{A cm}^{-2}$ was obtained for the electrolyte composition PEO:EC = 1:1 under the irradiation of 1000 W cm^{-2} .

The effect of incorporating Al_2O_3 filler on the properties of the plasticized electrolyte was studied using electrical and dielectric measurements, and thermal analysis. In the differential scanning calorimetry (DSC) thermograms the existence of two endothermic peaks was observed

on heating; one of these peaks is associated with the melting of the PEO crystallites, while the other peak at about 30 °C is associated with the melting of the EC rich phase. The temperature dependence of the conductivity exhibited an abrupt conductivity increase in the 1st heating run due to the melting of the EC rich phase. Conductivity isotherms showed the existence of two maxima, one at ~5 % Al₂O₃ content and the other at ~15 %. The occurrence of these two maxima could be explained in terms of the interactions caused by alumina grains and the crystallinity of the electrolyte. However, a conductivity enhancement could not be observed in the PEO/EC/ Pr₄N⁺I⁻ electrolyte due to incorporation of Al₂O₃ filler.

Enhanced ionic conductivity values were obtained for the ionic liquid tetrahexylammonium iodide containing PEO-based plasticized electrolytes. The conductivity measurements showed a marked conductivity enhancement during the melting of the plasticizer-rich phase of the electrolyte. Annealed electrolyte samples showed slightly better conductivity than non annealed samples revealing the existence of hysteresis. The optimum conductivity was shown for the electrolytes with PEO:Salt =100:15 mass ratio and this sample exhibited minimum T_g of -72.2 °C. For this optimum PEO:Salt ratio, the conductivity of non-annealed electrolyte was 4.4×10^{-4} S cm⁻¹ and that of the annealed sample was 4.6×10^{-4} at 30 °C. The short circuit current density (I_{sc}), open circuit voltage (V_{oc}) and power conversion efficiency (η %) of the PEC solar cell fabricated with optimum conductivity electrolyte are 0.63 mA cm⁻², 0.76 V and 0.47% under the irradiation of 600 W m⁻² light.

Gel polymer electrolytes based on PAN are potential candidates for photo-electrochemical solar cells. In this work, the plasticized gel polymer electrolyte PAN:EC:PC:MgI₂ was studied. At 20 °C the optimum ionic conductivity of 1.9×10^{-3} S cm⁻¹ was obtained for the (PAN)₁₀(MgI₂)_n(I₂)_{n/10}(EC)₂₀(PC)₂₀ electrolyte where $n = 1.5$. The predominantly ionic nature of the electrolyte is seen from the DC polarization data. DSC thermograms of electrolyte with different MgI₂ concentrations were studied and the glass transition temperatures were determined. The I - V characteristics revealed that the I_{sc} , V_{oc} and η of the cell are 3.87 mA cm⁻², 659 mV and 2.5 % respectively under the irradiation of 600 W m⁻².